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16. ABSTRACT

Inexpensive, reliable, accurate means are needed to monitor SO_2 and NO_2 in the atmosphere. Sulfation and nitration plates have been used with varying degrees of acceptance for two decades. These devices are exposed for a period of time where the pollutant in the surrounding ambient air reacts with the reactive surface of the monitor. The monitor is then returned to the laboratory where a chemical determination of the reaction product is made. By considering the duration of exposure and the reactive surface area, a product flux is determined. This product flux is used along with a calibration factor (CF) to estimate the gas-phase concentration of the pollutant. Historically this calibration factor, which relates ambient air pollutant concentration to product flux, has been assumed to be constant.

The objectives of this study are to evaluate the performance of commercial sulfation and nitration plates. The study is designed to determine the sensitivity of plate calibration factors to pollutant concentration, simulated wind speed, humidity, and temperature.

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EVALUATION OF THE PERFORMANCE OF SULFATION AND NITRATION PLATES

J. E. SICKLES, II and R. M. MICHIE
Research Triangle Institute, P.O.B. 12194, Research Triangle Park, North Carolina 27709, U.S.A.

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Abstract—Sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) are released in large quantities by anthropogenic sources. These gases are the major precursors of the acids which contribute to acidic deposition. Inexpensive, reliable and accurate means are needed to monitor SO_2 and NO_2 in the atmosphere.

One method which has been used with varying degrees of acceptance for two decades is the passive reactive monitor. Such a device is exposed for a period of time, and the pollutant in the surrounding ambient air reacts with the surface of the monitor. The reaction product is determined quantitatively, and a calibration factor is then applied to estimate the pollutant concentration in the ambient air averaged over the exposure period.

Passive monitors for SO_2 and NO_2, known as sulfation and nitration plates, are available from commercial suppliers. The object of the current study is to evaluate the performance of commercial sulfation and nitration plates. The study is designed to examine the sensitivity of plate calibration factors to pollutant concentration, simulated wind speed, humidity and temperature.

Test results indicate that for sulfation and nitration plates, sulfation calibration factors are extremely sensitive to wind speed. A slight effect of relative humidity was observed for sulfation calibration factors on both types of plates and for nitration calibration factors on nitration plates. Nitration calibration factors are extremely sensitive not only to wind speed, but also to NO_2 concentration and temperature. Additional work is needed to investigate the influence of humidity and temperature more thoroughly.

Key word index: Passive monitors, sulfur dioxide, nitrogen dioxide, deposition measurement, flux measurement, wind tunnel testing.

INTRODUCTION

Sulfur oxides and nitrogen oxides are released in large quantities by anthropogenic sources. Sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) are the major precursors of the acids which contribute to acidic deposition. Inexpensive, reliable, accurate means are needed to monitor these gases in the atmosphere.

One type of method which has been used with varying degrees of acceptance for over 50 years is the passive reactive monitor (Wilsdon and McConnell, 1934; Huey, 1968; A.P.H.A., 1977). Such a device is exposed for a period of time, and the pollutant in the surrounding ambient air reacts with the reactive surface of the monitor. The monitor is then returned to the laboratory for chemical determination of the reaction product. By considering the duration of exposure and the reactive surface area, a product flux (F) is determined. This product flux is used with a calibration factor (CF) to estimate the gas phase concentration of the pollutant (C). In some cases this calibration factor, which relates ambient air pollutant concentration to product flux ($CF = C/F$), has been assumed to be constant. The magnitude of this calibration factor may depend on several variables, such as pollutant concentration, wind speed, humidity and temperature (Lynch *et al.*, 1978).

Passive monitors for SO_2 and NO_2, known as sulfation and nitration plates, are available from commercial suppliers. The object of the current study is to evaluate the performance of commercial sulfation and nitration plates. The study is designed to examine the sensitivity of plate calibration factors to SO_2 and NO_2 concentrations, simulated wind speed, humidity and temperature.

METHODS

Experimental

An exposure apparatus was designed and built for the simultaneous exposure of up to 40 plates with half exposed at a high gas velocity and half at a low gas velocity. Plexiglas and stainless steel are the materials of construction. As indicated in Fig. 1, the test atmosphere is recirculated through the test section. Additionally, there are feed and bleed streams where the pollutant concentration is maintained at a constant level by controlling the pollutant flow rate into the feed stream. The test section is approximately 152 cm long, it contains two parallel channels, and each channel has dimensions of 6.35 by 10.2 cm. A baffle at the end of one channel effects the velocity difference. The test apparatus was contained in a temperature-controlled environmental chamber which can maintain the temperature to within $\pm 0.5°C$.

Air sampling occurs both up and downstream of the test section on a 30-min cycle as controlled by a Chrontrol timer. A Monitor Labs Model 8440 Nitrogen Oxides Analyzer and a Model 8450 Sulfur Monitor were used to determine the NO_2 and SO_2 concentrations in the test apparatus. The respective lower detectable limits (S/N ~ 2) are 10 and 9 ppb. An EG&G Model 880 was used to monitor dew point, and a shielded thermistor was used to measure temperature.

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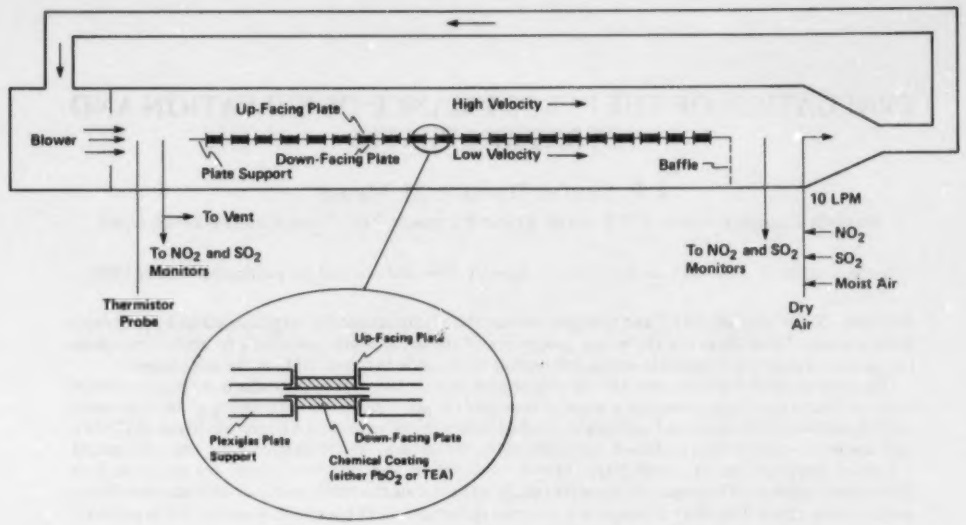

Fig. 1. Schematic of exposure apparatus.

A Thermo-Systems, Inc. Anemometer and a Datametric Barocel Electronic Manometer with a pitot tube were used to monitor gas velocity in the test section. In the high velocity (HV) channel the gas velocity at the centroid averaged 4.7 $m\,s^{-1}$, and in the low velocity (LV) channel the centroidal velocity averaged 0.67 $m\,s^{-1}$. Nominal Reynolds numbers in the two respective channels are 19,000 and 2700. Friction velocities were determined by two independent methods to be 0.18 and 0.21 $m\,s^{-1}$ in the HV channel and 0.024 and 0.040 $m\,s^{-1}$ in the LV channel.

Sulfation and nitration plates were purchased from a commercial source for testing. The sulfation plate is a 4.8-cm diameter (i.d.) Petri dish with an interior coating containing lead dioxide (PbO_2). The nitration plate is similar to the sulfation plate, except in this case the interior coating contains triethanolamine (TEA).

The experimental program is summarized in Table 1. Nominal pollutant concentrations of 20, 50 and 200 ppb were used. The tabulated concentration values represent means of hourly averages determined over the duration of each test.

Table 1. Summary of the experimental program

Test Number	Type	Mean concentration ppb	Mean concentration $\mu g\,m^{-3}$	CV,%	Test duration hr	Test duration day	Centroidal gas velocity ($m\,s^{-1}$) HV	Centroidal gas velocity ($m\,s^{-1}$) LV	Temperature °C	Relative humidity %
1	S*	53.9‡	141	91.0	250	10.4	4.57	0.684	25.8	48.1
	N†	0.0‡	0	§	250	10.4	4.57	0.684	25.8	48.1
2	S	0.0	0	§	166	6.92	4.66	0.693	26.4	42.1
	N	47.0	88.4	9.2	164	6.83	4.66	0.693	26.4	42.1
3	S	49.0	128	10.4	162	6.75	4.76	0.650	27.2	40.6
	N	51.0	95.9	6.7	162	6.75	4.76	0.650	27.2	40.6
4	S	207	541	5.1	144	6.00	4.73	0.667	26.0	45.5
	N	194	365	3.1	144	6.00	4.73	0.667	26.0	45.5
5	S	22.3	58.3	5.4	357	14.9	4.69	0.643	26.3	42.0
	N	21.6	40.6	10.6	357	14.9	4.69	0.643	26.3	42.0
6	S	50.5	131	3.2	144	6.00	4.90	0.678	26.0	78.7
	N	51.3	95.8	5.8	144	6.00	4.90	0.678	26.0	78.7
7	S	51.8	135	4.0	144	6.00	4.79	0.670	26.0	15.5
	N	50.6	94.5	10.5	144	6.00	4.79	0.670	26.0	15.5
8	S	50.1	140	2.2	144	6.00	4.60	0.644	5.6	48.2
	N	50.6	102	6.2	144	6.00	4.60	0.644	5.6	48.2

* Sulfation.
† Nitration.
‡ The species concentrations corresponding to S and N are for SO_2 and NO_2; the tabulated value is the mean of hourly average concentrations determined over the duration of the test.
§ Not available.

Except for the first test, a shakedown experiment, they exhibit good precision, generally better than 10%. Plates were exposed under test conditions for nominal periods of 1–2 weeks. Gas velocities of 4.7 and 0.7 m s^{-1} were used. In the first five exposures, nominal test conditions of 26°C and 45% relative humidity were employed. Tests 6 and 7 were conducted at the same temperature, but at different relative humidities—79 and 16%. Test 8 was conducted at a lower temperature, 5.6°C, and at 48% relative humidity.

The contents of each plate were removed and mixed with 50 ml of sodium bicarbonate–sodium carbonate IC eluent solution. The mixture was heated to 100°C for 30 min and allowed to cool. After filtration, the extract solutions were analyzed for nitrite (NO_2^-), nitrate (NO_3^-) and sulfate (SO_4^{2-}) by ion chromatography (IC).

IC analysis provides a direct measure of pollutant reaction product loading in units of μg/plate. By using the area per plate (18.1 cm^2) and the duration of exposure (day), the product flux in units of μg cm^{-2} day^{-1} is determined. The pollutant gas phase concentration is determined by the gas monitor and converted from ppb into μg m^{-3}. The calibration factor is the ratio of the gas concentration to the product flux. The reciprocal of the calibration factor (adjusted by the appropriate stoichiometry and molecular weight) may be expressed as the deposition velocity in cm s^{-1}

Quality assurance

The NO_x and SO_x analyzers were subjected to four-point calibrations before and after each test. At least one zero and span check was performed during each test.

The IC was calibrated daily. Independently prepared quality control samples were analyzed by IC along with regular samples. Difference analysis of the data showed the analyses to be unbiased with precision of 5% or better. Time series analysis showed no apparent trends.

Duplicate blank and spiked plates were extracted and analyzed. The extraction precision, as indicated by an average coefficient of variation for 16 paired measurements, is 2.6%. Analysis of spiked plates showed between 90 and 110% recovery of the added species.

Blank sulfation and nitration plates were analyzed. The background NO_2^-, NO_3^- and SO_4^{2-} levels on the tested plates differed from experiment to experiment. These levels on sulfation plates ranged respectively from 9, 44 and 19 μg/plate to 25, 200 and 268 μg/plate. The corresponding NO_2^-, NO_3^- and SO_4^{2-} levels for the tested nitration plates ranged from 18, 9 and 5 μg/plate to 39, 196 and 294 μg/plate. No lot-to-lot differences in background levels are apparent for either type of plate.

RESULTS

Blanks and exposed plates

Comparison of unexposed blank plate results with data from plates exposed during the first four experiments reveals several points of interest. Exposure of sulfation plates to NO_2 gives NO_2^-, NO_3^-, SO_4^{2-} loadings which do not differ appreciably from the background levels of the unexposed blank plates. This suggests that sulfation plates are essentially inert to NO_2. The addition of SO_2 to an NO_2 ladened gas mixture has no effect on the NO_2^- and NO_3^- loadings of sulfation plates.

Analysis of nitration plates exposed to NO_2 and NO_2–SO_2 mixtures indicates that NO_3^- loadings do not differ from the unexposed blanks, and deposited NO_2 is recovered as NO_2^-, not NO_3^-.

There was no humidity or temperature dependence for NO_2^- and NO_3^- loadings on sulfation plates or NO_3^- loadings on nitration plates. In addition, experiments where SO_2 was exposed to both nitration and sulfation plates show comparable SO_2 deposition on both types of plates.

Storage stability

Thirty plates exposed during the first three tests were selected, covered, and stored at room temperature for approximately 9 months. They were then analyzed in the usual manner. Results of the initial and final analyses were compared to determine the storage stability. On the average, an 11% deficit of SO_4^{2-} and a 32% deficit of NO_2^- were found for nitration plates after 9.5 months of storage. No appreciable difference in SO_4^{2-} was found for sulfation plates over the same period. Thus, nitration plates are more subject to storage problems than are sulfation plates.

Deposition gradient in test section

Results of plate analyses from the first test are shown in Fig. 2. The SO_4^{2-} concentration in the 50 ml of extract solution from each plate is given as a function of the plate's longitudinal position in the exposure apparatus. These results show: more SO_4^{2-} is deposited at HV than at LV; there is a substantial lot-to-lot difference in SO_4^{2-} deposition on sulfation plates; SO_2 deposition is comparable on sulfation and nitration plates; and a decreasing trend in deposition exists with position down the exposure apparatus which becomes negligible beyond position number seven. Increased deposition at high wind speeds has been observed by Wilsdon and McConnell (1934). The lot-to-lot effect is consistent with reported differences in PbO_2 reagent reactivity (A.P.H.A., 1977) and may be associated with PbO_2 particle size, although in the current study no lot-to-lot differences were apparent upon visual inspection. The 'position effect' is more pronounced at LV than HV and may reflect the sensitivity of deposition at LV to turbulence at the entrance to the test section. As a result of this finding, subsequent tests were conducted with dummy plates (having no chemical coating) in the first seven po-

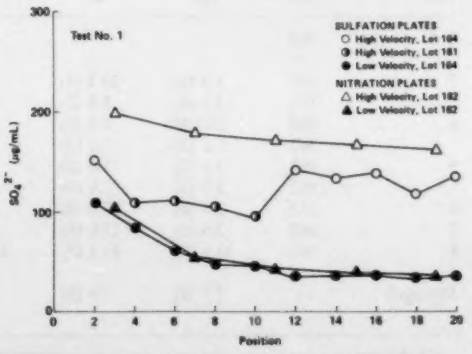

Fig. 2. Sulfate concentration in the desorption solution of each plate in Test No. 1 as a function of plate position.

sitions, and only the last 13 positions were used to expose authentic plates.

Product flux

Based on the plate analyses, product fluxes were determined and are given in Table 2. Since each of these entries is based on multiple plate exposures and analyses, the coefficient of variation (CV) and number of plate analyses upon which it is based were determined. These results are presented in Table 3. For the tests conducted at room temperature, on the average, the precision for determining NO_2 deposition is 3–8% while the precision for SO_2 deposition is 4–16%. These estimates are consistent with the CV of 12% reported for 47 paired sulfation plates exposed in the field (Vandenberg and Knoerr, 1983). The tabulated results also suggest that precision is dependent on velocity with the HV results having higher precision than the LV results, that nitration plates are slightly more precise than sulfation plates for quantifying SO_2 deposition, and that NO_2 deposition on nitration plates is more precise than SO_2 deposition on either sulfation or nitration plates.

The results in Table 3 also show that the precision of the NO_2 deposition determination is dependent on temperature. Much more variability is apparent at the lower temperature than at the higher temperature of the first seven experiments. In contrast, the precision of SO_2 deposition determination appears to be less sensitive to temperature. Examination of individual data revealed that the variability in the deposition determinations for Test 8 appears to be associated more with a trend related to position within the test apparatus than with random measurement error. The deposition decreases more strongly with distance down the chamber than in any of the earlier experi-

Table 2. Summary of flux data*

	Nitration plates					Sulfation plates		
		NO_2^-		SO_4^{2-}			SO_4^{2-}	
Test	Lot	HV	LV	HV	LV	Lot	HV	LV
1	162	—	—	43.46	10.05	164	35.38	10.29
	—	—	—	—	—	161	28.02	—
2	162	2.14	0.80	—	—	160	—	—
3	162	2.52	1.04	37.20	6.93	160	27.45	7.91
4	162	5.71	2.64	141.42	32.12	164	93.31	32.63
	163	5.56	2.58	141.08	31.62	161	68.14	26.16
5	162	1.67	0.65	16.40	4.04	164	13.55	4.04
	163	1.67	0.67	16.58	4.05	161	9.58	3.29
6	162	3.12	1.45	40.76	10.12	164	36.58	8.09
7	162	1.79	0.88	33.44	6.03	164	21.58	8.05
8	162	0.58	0.38	37.88	7.35	164	31.05	8.66

* Units = $\mu g\ cm^{-2}\ day$.

Table 3. Precision summary of plate determinations of product deposition*

	Nitration plates					Sulfation plates		
		NO_2^-		SO_4^{2-}			SO_4^{2-}	
Test	Lot	HV	LV	HV	LV	Lot	HV	LV
1	162	—	—	4.6 (4)	9.4 (3)	164	6.8 (5)	14.9 (7)
	—	—	—	—	—	161	7.1 (4)	—
2	162	3.9 (4)	10.3 (4)	—	—	160	—	—
3	162	3.7 (4)	4.3 (3)	3.5 (4)	10.6 (3)	160	8.8 (5)	20.7 (4)
4	162	2.9 (4)	6.0 (4)	3.2 (4)	18.2 (4)	164	5.5 (4)	22.3 (4)
	163	1.1 (2)	7.2 (2)	0.6 (2)	10.6 (2)	161	3.1 (2)	15.3 (2)
5	162	1.6 (5)	8.0 (5)	4.5 (5)	23.2 (5)	164	4.4 (4)	18.9 (4)
	163	1.5 (2)	3.9 (2)	5.0 (2)	4.2 (2)	161	2.4 (2)	7.3 (2)
6	162	3.4 (6)	7.0 (6)	2.3 (6)	14.2 (6)	164	5.8 (6)	11.5 (6)
7	162	3.6 (6)	13.0 (6)	4.6 (6)	23.0 (6)	164	4.2 (6)	18.0 (6)
8	162	33.9 (5)	42.2 (5)	12.3 (5)	28.1 (5)	164	10.8 (5)	17.9 (5)
Average†	—	2.7 (8)	7.5 (8)	3.5 (8)	14.2 (8)	—	5.3 (9)	16.1 (8)

* Tabulated entries are coefficients of variation in percent, and the entries in parentheses represent the number of plate determinations considered.

† Tabulated averages are for the tests performed at room temperatures; results from Test 8 are not included.

ments. This may be reflecting a change in the rate-controlling step of the deposition process with temperature reduction.

Calibration factors

The gas phase pollutant concentration data from Table 1 and the product flux data from Table 2 are combined to give a calibration factor ($CF = C/F$) for each test. The results are given in Table 4 and Figs 3 and 4.

Sulfation *CF* shown in Fig. 3 are independent of SO_2 concentration but are dependent on gas velocity across the plate and on lot-to-lot differences. As the SO_2 concentration varies by a factor of ten at a given velocity, the within-lot variation in the sulfation *CF* is relatively small. For the sulfation plates this variation is less than 25% as indicated by a coefficient of variation. For the nitration plates the variation is less than 15 %; and there is negligible difference across lots.

Differences in gas velocity exert a major influence on sulfation *CF*. The decrease in gas velocity by 86% from 4.7 to 0.7 $m\,s^{-1}$ results in an average increase of 4.45 ($\pm$ 11%) and 3.11 ($\pm$ 12%) in sulfation *CF* for nitration and sulfation plates.

Lot-to-lot variation is appreciable for sulfation plates but not for nitration plates. Sulfation plates from three lots were tested, although same-test comparisons could be drawn for only two lots. On the average, across five comparisons and three tests, the *CF* for sulfation plates from Lot 161 exceeds that from 164 by 30 %. Nitration plates from two lots (162 and 163) were tested. On the average, across four comparisons and two tests, the difference in sulfation *CF* is less than 1%.

Nitration *CF* shown in Fig. 4 are dependent on both NO_2 concentration and on gas velocity across the plate but are relatively independent of lot-to-lot differences. As the NO_2 concentration increases by an order of magnitude from 20 to 200 ppb, the *CF* increases by a factor of 2.3 at LV and by a factor of 2.7 at HV. It is unclear if the concentration dependence as seen in Fig. 4 should be extrapolated to the origin.

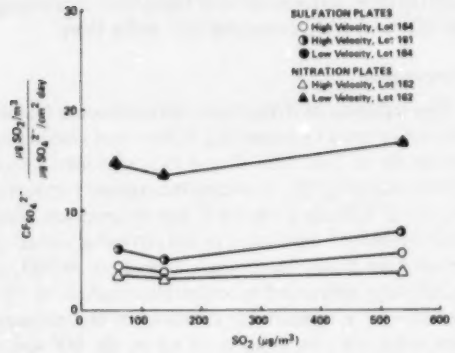

Fig. 3. Sulfation *CF* at two velocities for sulfation plates (Lot 164) and nitration plates (Lot 162) as a function of SO_2 concentration.

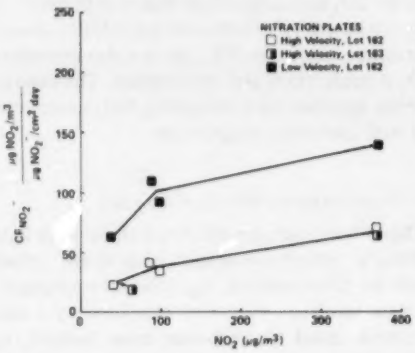

Fig. 4. Nitration *CF* at two velocities for nitration plates (Lot 162) as a function of NO_2 concentration.

Table 4. Summary of calibration factors

	Nitration plates							Sulfation plates			
		$CF_{NO_2^-}$*			$CF_{SO_4^{2-}}$‡				$CF_{SO_4^{2-}}$		
Test	Lot	HV	LV	Ratio†	HV	LV	Ratio	Lot	HV	LV	Ratio
1	162	—	—	—	3.20	13.8	4.33	164	3.98	13.7	3.44
	—	—	—	—	—	—	—	161	5.04	—	—
2	162	41.3	109.7	2.68	—	—	—	160	—	—	—
3	162	38.0	92.1	2.41	3.44	18.5	5.36	160	4.66	16.2	3.47
4	162	63.9	138.1	2.16	3.82	16.9	4.40	164	5.80	16.6	2.86
	163	65.7	141.7	2.16	3.84	17.1	4.46	161	7.94	20.7	2.60
5	162	24.3	62.5	2.57	3.55	14.5	4.06	164	4.30	14.5	3.35
	163	24.3	60.5	2.49	3.52	14.4	4.09	161	6.09	17.7	2.91
6	162	30.6	65.8	2.15	3.21	12.9	4.03	164	3.58	16.2	4.51
7	162	52.8	106.8	2.02	4.04	22.4	5.55	164	6.26	16.8	2.68
8	162	175.2	267.9	1.53	3.70	19.0	5.15	164	4.51	16.2	3.58

* $CF_{NO_2^-}$ = Concentration [$\mu g\ NO_2\ m^{-3}$]/flux [$\mu g\ NO_2^-\ cm^{-2}\ day^{-1}$].
† Ratio = *CF* at LV/CF at HV.
‡ $CF_{SO_4^{2-}}$ = Concentration [$\mu g\ SO_2\ m^{-3}$]/flux [$\mu g\ SO_4^{2-}\ cm^{-2}\ day^{-1}$].

The decrease in gas velocity from 4.7 to 0.7 m s^{-1} results in an average increase of 2.4 in the *CF*. This increase is relatively insensitive to NO_2 concentration and is constant to within 9% over an order of magnitude change in NO_2 concentration.

Nitration plates from two lots were tested. As indicated in Fig. 4, the lot-to-lot variation is small. On the average, across four comparisons and two tests, the difference in nitration *CF* was less than 3%.

Deposition velocities

Calibration factors from Table 4 can be converted to deposition velocities. Deposition velocity is proportional to the reciprocal of the *CF* where the proportionality constant accounts for reaction stoichiometry and the conversion of days to seconds. The deposition velocity for SO_2 ranges from 0.35 to 2.4 cm s^{-1}. It is comparable for both sulfation and nitration plates, it increases with velocity, but at fixed simulated wind speeds it is independent of SO_2 concentration.

The deposition velocity for NO_2 is much less than that for SO_2 and ranges from 0.04 to 0.48 cm s^{-1}. Not only is it strongly dependent on gas velocity, as was the deposition velocity for SO_2, but it is also dependent on NO_2 concentration and temperature. The deposition velocity increases with decreasing NO_2 concentration and with increasing temperature.

Chamber-averaged deposition velocities

Deposition velocities discussed above were used to determine chamber-averaged deposition velocities based on plate analyses, v_{dP}. Chamber-averaged deposition velocities were also estimated by a second technique based on pollutant mass balance, v_{dMB}. Pollutant deposition rates were determined for the exposure apparatus in the presence and absence of plates, based on mass balance considerations and measured gas phase pollutant concentrations. The pollutant deposition rate to the plates was then determined by difference. The overall flux was determined from the deposition rate to the exposed reactive plates and their total surface area. The overall flux was divided by the pollutant gas concentration to give an estimate of the chamber-averaged deposition velocity, v_{dMB}. These estimates are independent of the IC determination of pollutant deposition to the plates and the resulting v_{dP}.

The mass balance approach involves using the difference between two measured values. The measured differences in SO_2 concentrations with and without plates (400 and 60 ppb) were much larger than the corresponding values for NO_2 (30 and 9 ppb). In general, this approach potentially has more opportunity for error than the more direct approach using plate analysis. The agreement is nevertheless good for the chamber-averaged deposition velocities based on plate analysis and on mass balance. Except for the low temperature test, v_{dMB} exceeds the v_{dP}, on the average, by 28 ± 10%.

Relative humidity

The influence of different relative humidities on calibration factors was investigated in high and low velocity tests. These results indicate that with one exception, nitration and sulfation *CF* increase appreciably with decreased humidity. Since only a single comparison is available, attempts at discriminating the interactions of humidity, velocity and plate type on *CF* are not warranted. Thus, the impact of humidity is examined only in an average sense. As the relative humidity decreases from 79 to 16%, the calibration factors increase by an average of 52 ± 30%.

This humidity effect can be viewed with more physical significance by considering its influence on deposition velocity rather than *CF*. Thus, increasing the humidity by five-fold increases the deposition velocities of SO_2 and NO_2 to the tested surfaces by approximately 50%. This suggests that moist collection surfaces under high humidities are more effective than the drier surfaces of lower humidities at retaining the SO_2 and NO_2 molecules that strike them.

Temperature

The influence of temperature on calibration factors may be inferred by inspecting Table 4 and comparing the results of Test 3 (27°C and 41% r.h.) with Test 8 (5.6°C and 48% r.h.). Reducing the exposure temperature by 22°C from 27 to 5.6°C has no apparent effect on the averaged deposition of SO_2 to either nitration or sulfation plates. In contrast, deposition of NO_2 is significantly influenced by temperature reduction. The nitration *CF* is appreciably increased by the temperature reduction—by a factor of 4.6 at the HV and a factor 2.9 at the LV. This temperature reduction results in a 78% reduction in the deposition velocity at HV and a 66% reduction at LV. The temperature sensitivity of the nitration plates may be reflecting the liquid-to-solid phase change that occurs for TEA around 21°C.

CONCLUSIONS

The performance of commercially available passive monitors for SO_2 and NO_2 has been evaluated. SO_2 is collected as SO_4^{2-} on both sulfation and nitration plates. NO_2 is collected effectively only on the nitration plates and is retained as NO_2^-. Nitration plates are subject to SO_4^{2-} and NO_2^- loss during storage and should be analyzed promptly after use. No SO_4^{2-} loss was observed for sulfation plates.

The percentage changes in calibration factors (*CF*) corresponding to changes in the tested environmental variables are given in Table 5 along with precision estimates. Sulfation *CF*, for both types of plates, are relatively independent of SO_2 concentration and temperature. They are dependent on wind speed and

Table 5. Summary of the sensitivity and precision of calibration factors for sulfation and nitration plates

Plate type	Calibration factor	Percentage change in *CF* corresponding to indicated change of environmental variable: Concentration 20–200 ppb	Wind speed 4.7–0.7 m s^{-1}	Humidity 79–16% r.h.	Temperature 27–5.6°C	Precision (%): Lot-to-lot	Plate-to-plate within-lot
Sulfation	$CF_{SO_4^{2-}}$	±25	+310	+39	negligible*	±30	±5.3† ±16‡
Nitration	$CF_{SO_4^{2-}}$	±15	+450	+49	negligible*	negligible*	±3.5† ±14‡
Nitration	$CF_{NO_3^-}$	+250	+240	+67	+460† +290‡	negligible*	±2.7† ±7.5‡

* On the average the difference is less than 5%.
† Result is for the high velocity wind speed.
‡ Result is for the low velocity wind speed.

relative humidity. For sulfation plates the *CF* are subject to appreciable lot-to-lot differences and to smaller plate-to-plate within-lot differences. As the simulated wind speed was reduced from 4.7 to 0.7 m s^{-1}, the sulfation *CF* increased by factors of 3.1 and 4.5 on sulfation and nitration plates. As the relative humidity was reduced from 79 to 16%, this *CF* increased on the average by 45% for sulfation and nitration plates. The lot-to-lot precision of SO_2 deposition to nitration plates was better than 1%; while for sulfation plates this difference averaged 30%. At room temperature, the plate-to-plate within-lot variability of SO_2 deposition to sulfation and nitration plates averaged 4.5% at the high velocity test condition and 15% at the low velocity test condition.

Nitration *CF* are sensitive to most of the tested variables. As the NO_2 concentration was increased from 20 to 200 ppb, the *CF* increased by a factor of 2.5. As the simulated wind speed was reduced from 4.7 to 0.7 m s^{-1}, the *CF* increased by a factor of 2.4. Reducing the relative humidity from 79 to 16% increased the nitration *CF* by 67%. A temperature change from 27°C to 5.6°C increased the *CF* by a factor of 4.6 at the higher wind speed and 2.9 at the lower wind speed.

The lot-to-lot variation in nitration *CF* is small and was found to be less than 3%. At room temperature the plate-to-plate within-lot variability of NO_2 deposition to nitration plates averaged 2.7% at the high wind speed and 7.5% at the lower wind speed.

Test results indicate that for either sulfation or nitration plates, sulfation *CF* are extremely sensitive to wind speed. Nitration *CF* are extremely sensitive not only to wind speed, but to NO_2 concentration and temperature as well. Additional work is needed to investigate the impact of humidity and temperature on calibration factors.

These findings identify and quantify many of the uncertainties associated with the use of sulfation or nitration plates in ambient air quality monitoring. They should provide insight toward the interpretation of data collected using such devices. Finally, these results should provide guidance as to the quality of information that can be expected from these devices if their deployment is considered in future air quality studies.

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